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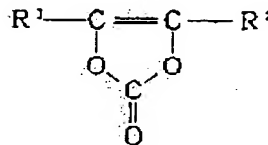
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(54) NONAQUEOUS ELECTROLYTE AND NONAQUEOUS ELECTROLYTE SECODARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve incombustibility, a generated voltage and battery charge/ discharge performances by including a specific vinylene carbonate derivative and a phosphate compound in a nonaqueous solvent formed together with an electrolyte.

SOLUTION: A vinylene carbonate derivative is shown by a formula and included by 0.001 wt.% or more, preferably 0.1-5 wt.%. A phosphate compound, added by 0.1 wt.% or more for imparting incombustibility, has preferably an alkyl group or a fluorine-substituted alkyl group or the like having a carbon number of one to six, especially preferably trimethyl phosphate. Besides, charge/discharge efficiencies and load characteristics are improved, and also electric conductivity of an electrolyte and self-quenching property are improved, by including one or more cyclic or chain carbonic acid ester in a nonaqueous solvent. Preferably, lithium or the like is used as a negative-electrode active material, and a complex oxide of lithium and a transition metal is used as a positive-electrode active material. [In the formula, R1 and R2 are hydrogen or 1-3C alkyl groups, and may be the same].



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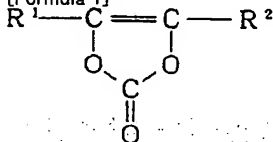
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CLAIMS

[Claim(s)]

[Claim 1] Nonaqueous electrolyte characterized by the bird clapper from the non-aqueous solvent containing the vinylene carbonate derivative expressed with the following general formula [I], and a phosphoric ester compound, and an electrolyte.

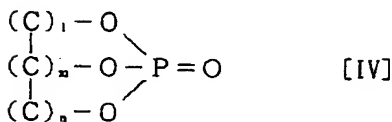
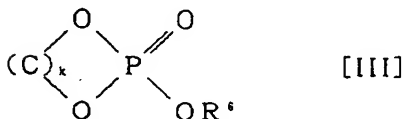
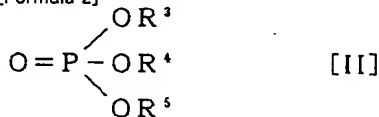
[Formula 1]



(Among a formula, even if R1 and R2 are mutually the same, they may differ from each other, and they show a hydrogen atom or the alkyl group of carbon numbers 1-3.)

[Claim 2] Nonaqueous electrolyte according to claim 1 characterized by the aforementioned phosphoric ester compound being phosphoric ester expressed with following general formula [II] - [IV].

[Formula 2]



(Among a formula, even if R3-R6 are mutually the same, they may differ from each other, and they show the alkyl group or fluorine substitution alkyl group of carbon numbers 1-6.) - (C)- is the hydrocarbon group of the shape of a straight chain, and the letter of branching, k, l, m, and n show a carbon number, k is the integer of 2-8, and at least one of l, m, and the n is [it may differ, even if l, m, and n are mutually the same, and it is the integer of 0-12, and] one or more integers.

[Claim 3] Nonaqueous electrolyte according to claim 1 or 2 to which the aforementioned phosphoric ester compound is characterized by being trimethyl phosphate.

[Claim 4] Nonaqueous electrolyte according to claim 1 to 3 characterized by the aforementioned non-aqueous solvent containing further at least one sort of carbonates chosen from an annular carbonate and a chain-like carbonate.

[Claim 5] The nonaqueous electrolyte rechargeable battery characterized by having nonaqueous electrolyte according to claim 1 to 4 as a lithium, the positive electrode containing the multiple oxide of transition metals, and the electrolytic solution as the negative electrode which contains a metal lithium, a lithium content alloy, or the carbon material in which the dope and ** dope of a lithium ion are possible as a negative-electrode active material, and a positive active material.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] this invention relates to the nonaqueous electrolyte rechargeable battery containing this electrolytic solution while relating to the nonaqueous electrolyte which it is still more detailed, and fire retardancy is high, was safe, and could generate the high voltage, and was excellent in cell charge/discharge capability ability about nonaqueous electrolyte and a nonaqueous electrolyte rechargeable battery.

[0002]

Background of the Invention] Nonaqueous electrolyte is used as the electrolytic solution of energy-storage devices, such as a lithium cell and an electric double layer capacitor, and since these devices have a high voltage and high-energy density and are excellent in reliability, they are widely used for the power supply of consumer electronics etc. Nonaqueous electrolyte consists of a non-aqueous solvent and an electrolyte, and propylene carbonate [which is generally the organic solvent of a high dielectric constant], gamma-butyrolactone, sulfolane or dimethyl carbonate that is the organic solvent of hypoviscosity], dimethoxyethane, tetrahydrofuran, 1, and 3-dioxolane etc. is used as a non-aqueous solvent. Moreover, as an electrolyte, Et4NBF4, LiBF4, LiPF6, LiClO4 and LiAsF6, LiCF3SO3, LiAlCl4, LiSiF6, etc. are used.

[0003] By the way, since a cell with a high energy density is desired, research is advanced about the high-voltage cell. For example, the rechargeable battery called rocking-chair type which used the lithium of LiCoO2, LiNiO2, and LiMn2O4 grade and the multiple oxide of transition metals for the positive electrode of a cell, and used the carbon material for the negative electrode is studied. since [in this case,] a cell voltage can generate more than 4V and moreover does not have a deposit of a metal lithium -- overcharge and external short-circuit -- ****(ing) -- crushing -- etc. -- also by experiment, it is checked that safety is secured and it appears on the market as a noncommercial use. However, when the future large formation of high-energy density and enlargement are made, to raise safety further is desired and it is called for that inflammable nonaqueous electrolyte has self-extinguishing.

[0004] For this reason, adding the phosphoric ester known as a compound with self-extinguishing to the electrolytic solution is proposed (for example, refer to JP,4-184870,A).

[0005] However, although the electrolytic solution which added general phosphoric ester, such as phosphoric-acid triethyl, is fire retardancy and safety improved, depending on the kind and addition of phosphoric ester, there were also cell charge-and-discharge efficiency, an energy density of a cell, and a thing that cannot necessarily be satisfied in respect of a battery life.

[0006]

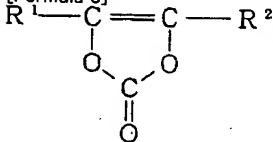
[Objects of the Invention] this invention aims at offering the rechargeable battery containing this nonaqueous electrolyte while it aims at offering the nonaqueous electrolyte which was made in view of the above-mentioned trouble, fire retardancy was highly safe, and could generate the high voltage, and was excellent in cell charge/discharge capability ability.

[0007]

[Summary of the Invention] The nonaqueous electrolyte concerning this invention is characterized by the bird clapper from the non-aqueous solvent containing the vinylene carbonate derivative expressed with the following general formula [I], and a phosphoric ester compound, and the electrolyte.

[0008]

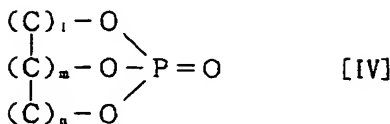
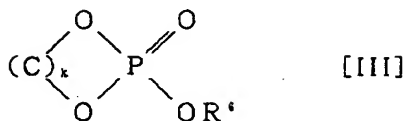
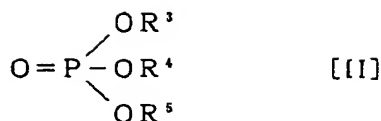
[Formula 3]



[0009] (Among a formula, even if R1 and R2 are mutually the same, they may differ from each other, and they show a hydrogen atom or the alkyl group of carbon numbers 1-3.)

It is desirable that the aforementioned phosphoric ester compound is phosphoric ester expressed with following general formula [II] - [IV], and it is [0010].

[Formula 4]



[0011] (Among a formula, even if R3-R6 are mutually the same, they may differ from each other, and they show the alkyl group or fluorine substitution alkyl group of carbon numbers 1-6.) - (C)- is the hydrocarbon group of the shape of a straight chain, and the letter of branching, k, l, m, and n show a carbon number, k is the integer of 2-8, and at least one of l, m, and the n is [it may differ, even if l, m, and n are mutually the same, and it is the integer of 0-12, and] one or more integers. It is desirable especially that it is trimethyl phosphate.

[0012] As for the aforementioned non-aqueous solvent, it is desirable that at least one sort of an annular carbonate and a chain-like carbonate is included further. The nonaqueous electrolyte rechargeable battery concerning this invention is characterized by the lithium, the positive electrode containing the multiple oxide of transition metals, and having the aforementioned nonaqueous electrolyte as the electrolytic solution as the negative electrode which contains a metal lithium, a lithium content alloy, or the carbon material in which the dope and ** dope of a lithium ion are possible as a negative-electrode active material, and a positive active material.

[0013]

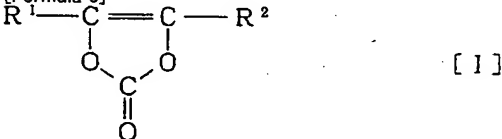
[Detailed Description of the Invention] Hereafter, the nonaqueous electrolyte concerning this invention and the nonaqueous electrolyte rechargeable battery using this nonaqueous electrolyte are explained concretely.

[0014] The nonaqueous electrolyte concerning this invention consists of a non-aqueous solvent containing a specific vinylene carbonate derivative and a specific phosphoric ester compound, and an electrolyte.

What is expressed with the following general formula [I] as a vinylene carbonate derivative used by the vinylene carbonate derivative this invention is used.

[0015]

[Formula 5]



[0016] (Among a formula, even if R1 and R2 are mutually the same, they may differ from each other, and they show a hydrogen atom or the alkyl group of carbon numbers 1-3.)

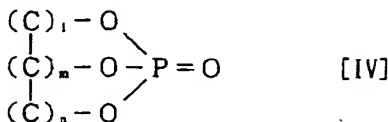
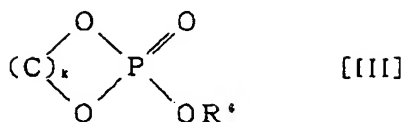
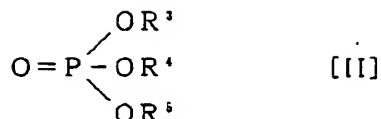
As such a vinylene carbonate derivative, vinylene carbonate, 4, 5-dimethyl vinylene carbonate, 4, 5-diethyl vinylene carbonate, 4, 5-dipropyl vinylene carbonate, 4-ethyl-5-methyl vinylene carbonate, 4-ethyl-5-propyl vinylene carbonate, 4-methyl-5-propyl vinylene carbonate, etc. are mentioned.

[0017] There is an effect of improving the charge-and-discharge efficiency of the cell produced in case a phosphoric ester compound is added, and the fall of a load characteristic in such a vinylene carbonate derivative.

As a phosphoric ester compound used by the phosphoric ester compound this invention, the phosphoric ester expressed with following general formula [II] - [IV] is used preferably.

[0018]

[Formula 6]



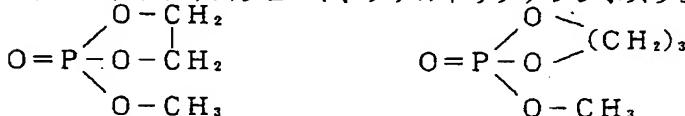
[0019] (Among a formula, even if R3-R6 are mutually the same, they may differ from each other, and they show the alkyl group or fluorine substitution alkyl group of carbon numbers 1-6.) - (C)- is the hydrocarbon group of the shape of a straight chain, and the letter of branching, k, l, m, and n show a carbon number, k is the integer of 2-8, and at least one of l, m, and the n is [it may differ, even if l, m, and n are mutually the same, and it is the integer of 0-12, and] one or more integers.

Specifically as phosphoric ester expressed with a formula [II], trimethyl phosphate, triethyl phosphate, TORIPURO pill phosphate, tributyl phosphate, dimethyl ethyl phosphate, methyl diethyl phosphate, etc. are mentioned.

[0020] Specifically as phosphoric ester expressed with a formula [III], it is [0021].

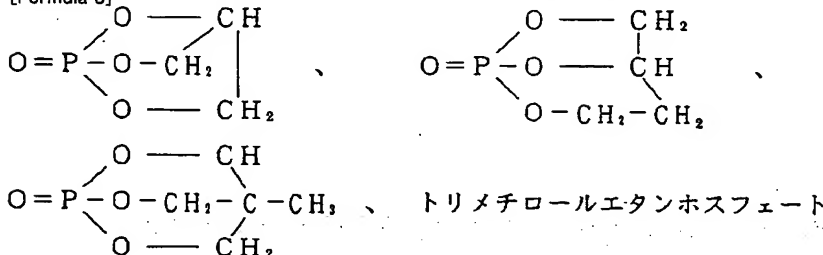
[Formula 7]

メチルエチレンホスフェート、メチルトリメチレンホスフェート



[0022] **** is mentioned. Specifically as phosphoric ester expressed with a formula [IV], it is [0023].

[Formula 8]



[0024] **** is mentioned. In respect of fire-resistant grant, since the effect is large, trimethyl phosphate and phosphoric-acid triethyl are desirable, and especially trimethyl phosphate is [among these] desirable.

[0025] In the nonaqueous electrolyte concerning a non-aqueous-solvent this invention, the non-aqueous solvent containing the above vinylene carbonate derivatives and a phosphoric ester compound is used.

[0026] As for the aforementioned phosphoric ester compound, it is preferably desirable one to 40 volume % and to be contained in the amount of 3 - 25 volume % still more preferably in a non-aqueous solvent more than 0.1 volume %. If the phosphoric ester compound is contained in the non-aqueous solvent in such an amount, sufficient fire retardancy for nonaqueous electrolyte can be given.

[0027] Moreover, the non-aqueous-solvent pair of the aforementioned vinylene carbonate derivative is carried out, and it is preferably desirable to be added in 0.1 - 5% of the weight of the amount still more preferably 0.01 to 20% of the weight 0.001% of the weight or more. The charge-and-discharge efficiency of the cell produced in case a phosphoric ester compound will be added, if the vinylene carbonate derivative is added in the non-aqueous solvent in such an amount, and the fall of a load characteristic are fully improvable.

[0028] It is desirable to contain carbonates, such as an annular carbonate and chain-like carbonate, in the non-aqueous solvent used by this invention in addition to a vinylene carbonate derivative and a phosphoric ester compound. By including such a carbonate, the charge-and-discharge efficiency and the load characteristic of a cell are further improvable.

[0029] As an annular carbonate, ethylene carbonate, propylene carbonate, butylene carbonate, etc. are mentioned. these — one sort — or two or more sorts may use it, mixing The mixed solvent of ethylene carbonate, propylene carbonate or ethylene carbonate, and propylene carbonate is preferably used among these annular carbonates. If the

annular carbonate is contained, it is possible to raise the solubility of the electrolyte in low temperature, transportation of an electrolyte can become easy, and the electrical conductivity of the electrolytic solution can be raised further.

[0030] As a chain-like carbonate, dimethyl carbonate, methylethyl carbonate, diethyl carbonate, methylpropyl carbonate, methyl isopropyl carbonate, ethyl propyl carbonate, etc. are mentioned. these — one sort — or two or more sorts may use it, mixing. Since dimethyl carbonate can raise the self-extinguishing of the electrolytic solution among these chain-like carbonates, it is desirable. If these chain-like carbonates are contained in the non-aqueous solvent, it is possible to make viscosity of nonaqueous electrolyte low, and electrolytic solubility can be raised further and it can consider as the electrolytic solution excellent in the electrical conductivity in ordinary temperature or low temperature.

[0031] The above chain-like carbonates and annular carbonates can also be mixed and used. such a carbonate — the non-aqueous-solvent whole quantity — receiving — ten to 99 volume % — it is preferably desirable 40 to 97 volume % and to be contained in the amount of 80 – 97 volume % still more preferably

[0032] If it is possible to raise the electrical conductivity of nonaqueous electrolyte if the annular carbonate is contained in the non-aqueous solvent in such an amount and the chain-like carbonate is contained, nonaqueous electrolyte excellent in self-extinguishing can be obtained.

[0033] In the non-aqueous solvent used by this invention further again, the above-mentioned phosphoric ester, a vinylene carbonate derivative, The methyl formate usually used as a non-aqueous solvent for cells besides an annular carbonate and chain-like carbonate, An ethyl formate, a propyl formate, methyl acetate, ethyl acetate, propyl acetate, Chain-like ether, such as chain-like ester, such as a methyl propionate and an ethyl propionate, and dimethoxyethane, Amides, such as cyclic ether, such as a tetrahydrofuran, and a dimethylformamide Methyl – Chain-like carver mates, such as N and N-dimethyl carver mate Annular sulfones, such as cyclic ester, such as gamma-butyrolactone, and a sulfolane Non-aqueous solvents, such as annular ureas, such as cyclic-amides [such as annular carver mates, such as N-methyl oxazolidinone and N-methyl pyrrolidone,], N, and N-dimethyl imidazolidone, etc. can be used.

[0034] As an electrolyte which is dissolving into electrolyte nonaqueous electrolyte For example LiPF₆, LiBF₄, LiClO₄, LiAsF₆, LiCF₃SO₃, LiN (SO₂CF₃)₂, LiN (SO₂C₂F₅)₂, LiC (SO₂CF₃)₃, LiN (SO₃CF₃)₂, LiN (SO₃CH₂CF₃)₂, LiAlCl₄, LiSiF₆, Lithium salt, such as LiC₄F₉SO₃ and LiC₈F₁₇SO₃, is mentioned. These lithium salt may be used independently, and may mix and use two or more sorts of lithium salt.

[0035] Since LiPF₆ and LiBF₄ become [fire retardancy] high by the synergism with phosphoric ester among these lithium salt, it is used preferably. As for such an electrolyte, it is usually desirable to contain 0.1–3 mols /in nonaqueous electrolyte by the concentration of 0.5–2 mols/l. preferably.

[0036] The nonaqueous electrolyte rechargeable battery concerning a nonaqueous electrolyte rechargeable battery this invention consists of a lithium, a positive electrode containing the multiple oxide of transition metals, and aforementioned nonaqueous electrolyte as the negative electrode which contains a metal lithium, a lithium content alloy, or the carbon material in which the dope and ** dope of a lithium ion are possible as a negative-electrode active material, and a positive active material.

[0037] Such a nonaqueous electrolyte rechargeable battery is applicable to for example, a cylindrical nonaqueous electrolyte rechargeable battery. It comes to contain a cylindrical nonaqueous electrolyte rechargeable battery with the cell can 5, where an electric insulating plate 4 is laid in the upper and lower sides of winding and a winding object through the separator 3 into which nonaqueous electrolyte was poured for the negative electrode 1 which applies a negative-electrode active material to the negative-electrode charge collector 9, and becomes it as shown in drawing 1, and the positive electrode 2 which comes to apply a positive active material to the positive-electrode charge collector 10. the cell can 5 — the cell lid 7 — the obturation gasket 6 — minding — by closing, it is attached and connects with a negative electrode 1 or a positive electrode 2 electrically through the negative-electrode lead 11 and the positive-electrode lead 12, respectively, and it is constituted so that it may function as the negative electrode or positive electrode of a cell. In addition, separator is a porous film.

[0038] By this cell, as for the positive-electrode lead 12, electrical installation with the cell lid 7 may be measured through the sheet metal 8 for current interception. By such cell, if the pressure inside a cell rises, the sheet metal 8 for current interception is pushed up, and deforms, the positive-electrode lead 12 leaves the above-mentioned sheet metal 8 and the welded portion, and is cut, and current has become as [intercept / current].

[0039] Although any of the carbon material as a negative-electrode active material which constitutes such a negative-electrode 1 which can dope and ** dope a metal lithium, a lithium alloy, and a lithium ion can be used, it is desirable to use the carbon material which can dope and ** dope a lithium ion among these. Such a carbon material may be an amorphous carbon even if it is graphite, and all carbon materials, such as activated carbon, a carbon fiber, carbon black, and a meso carbon micro bead, are used.

[0040] Especially in this invention, the spacing (d002) of the field (002) measured with X-ray analysis is 0.37nm or less, and if the carbon material which has a property near the graphite whose density is three or more 1.70 g/cm³ is desirable and uses such a carbon material, the energy density of a cell can be made high.

[0041] Moreover, the multiple oxide which the multiple oxide which consists of the lithium and transition metals of transition-metals oxides, such as MoS₂, TiS₂, MnO₂, and V₂O₅, and a transition-metals sulfide or LiCoO₂ and LiMnO₂, LiMn₂O₄, and LiNiO₂ grade is used as a positive active material which constitutes a positive electrode 2, and especially consists of a lithium and transition metals is desirable.

[0042] Moreover, the nonaqueous electrolyte rechargeable battery concerning this invention is applicable also to a coin type nonaqueous electrolyte rechargeable battery as shown in drawing 2. with the coin type nonaqueous electrolyte rechargeable battery of drawing 2, the disk-like negative electrode 13, the disk-like positive electrode 14, separator 15, and the stainless board 17 contain with the cell can 16, where a laminating is carried out in the sequence of the stainless board 17, a negative electrode 13, separator 15, a positive electrode 14, and — having — the cell can (lid) 19 — a gasket 18 — minding — it is attached by closing The same thing as the above is used as a negative electrode 13, separator 15, and a positive electrode 14. Moreover, the thing of the quality of the material of the stainless steel which cannot corrode the cell can 16 and the cell can (lid) 19 easily due to the electrolytic solution is used.

[0043] In addition, it may not be limited to what showed the configuration of a cell etc. to drawing 1 and drawing 2 including the nonaqueous electrolyte which explained the nonaqueous electrolyte rechargeable battery concerning this invention above as the electrolytic solution, but you may be a square shape etc.

[0044]

[Effect of the Invention] The nonaqueous electrolyte concerning this invention is fire retardancy, and excellent in charge/discharge capability ability, and the nonaqueous electrolyte rechargeable battery using such nonaqueous electrolyte is safe, can generate the high voltage, and is excellent in a charge-and-discharge property.

[0045]

[Example] Although an example is given and this invention is explained concretely hereafter, this invention is not limited at all by these examples.

[0046]

[Example 1] After dissolving <manufacture of nonaqueous electrolyte> LiPF₆15.2g (100mmol) in the mixed solvent (mixture product ratio EC:DMC:TMPA= 33.25:61.75:5.0) of ethylene carbonate (EC), dimethyl carbonate (DMC), and trimethyl phosphate (TMPA), it added so that the vinylene carbonate concentration in nonaqueous electrolyte might become 0.1 % of the weight, and nonaqueous electrolyte was prepared (electrolyte concentration of 1.0 mols/l.).

[0047] <production of a negative electrode> — the negative electrode 13 was produced as follows first 95 weight-sections and the polyvinylidene-fluoride (PVDF) 5 weight section of a binder are mixed in the carbon-powder end of the mezzo-soprano phase PITCHIMAKUIRO fiber Made from PETOKA (tradename : mel BUROMMIRUDO, d 002= 0.336nm, density 2.21 g/cm³), and it distributes to N-methyl pyrrolidone of a solvent — making — a negative electrode — a mixture — the slurry (the shape of a paste) was prepared

[0048] this negative electrode — a mixture — the slurry was applied to the negative-electrode charge collector with a thickness of 20 micrometers made from band-like copper foil, and the dried band-like carbon electrode was obtained such a carbon electrode — the thickness of a mixture was 25 micrometers After piercing this band electrode with a diameter of 15mm in the shape of a disk furthermore, it pressed and considered as the negative electrode 13.

[0049] The <production of positive electrode> positive electrode 14 was produced as follows. the LiCoO₂ (21.8 micrometers of mean particle diameters [Product name : HLC-]) 91 weight section by Honjo Chemical, the graphite. 6 weight section of electric conduction material, and the polyvinylidene-fluoride 3 weight section of a binder — mixing — a positive electrode — preparing a mixture and distributing N-methyl pyrrolidone — a positive electrode — a mixture — the slurry was obtained

[0050] The positive-electrode charge collector made from a band-like aluminum foil with a thickness of 20 micrometers was made to apply and dry this slurry, it pressed, and the band-like positive electrode was obtained. ***** of such a positive electrode was 40 micrometers. It considered as the positive-electrode electrode 14 by furthermore piercing this band electrode with a diameter of 15mm in the shape of a disk.

[0051] <production of a cell> — as shown in drawing 2, after carrying out the laminating of the disk-like negative electrode 13 obtained by doing in this way, the disk-like positive electrode 14, and the separator 15 (micrometers [in thickness / 25], fine porosity polypropylene film with a diameter of 19mm) to the cell can 16 of 2032 sizes made from stainless steel in the sequence of a negative electrode 13, separator 15, and a positive electrode 14, the aforementioned nonaqueous electrolyte was poured into separator 15 Then, after containing the board 17 (the thickness of 2.4mm, diameter of 15.4mm) made from stainless steel, through the gasket 18 made from polypropylene, by closing the cell can (lid) 19, the airtightness in a cell was held and the button type nonaqueous electrolyte rechargeable battery with a diameter [of 20mm] and a height of 3.2mm was produced.

[0052] <measurement of service capacity and a load characteristic> — the service capacity of the nonaqueous electrolyte rechargeable battery which carried out in this way and was produced was measured In addition, in this example, the direction of current where Li⁺ is doped by the negative electrode was considered as charge, and the direction of current by which a ** dope is carried out was considered as charge.

[0053] Charge was performed by the 4.2V or 1mA constant-current constant-voltage method, and when the charging current became below 50microA, it considered as the end. Electric discharge was performed by the 1mA constant current, and when voltage amounted to 2.7V, it considered as the end. From the charge capacity of this charge-and-discharge cycle, and service capacity, charge-and-discharge efficiency was measured by the following formula. A result is shown in Table 1.

[0054]

[Equation 1]

$$\text{充放電効率 (\%)} = \frac{\text{放電容量 (mAh/g)}}{\text{充電容量 (mAh/g)}} \times 100$$

[0055] The Manila paper for separators with a thickness of 0.04mm cut with a length of 30cm 15mm and in the shape of a strip of paper in the beaker containing the <self-extinguishing evaluation of nonaqueous electrolyte> aforementioned nonaqueous electrolyte was dipped 1 minute or more. The superfluous nonaqueous electrolyte which drips from Manila paper was wiped with the beaker wall, the support needle of the sample base which has a support needle at intervals of 2.5cm was stabbed with Manila paper, and it fixed horizontally. The sample base which fixed Manila paper was put into the 25cmx25cmx50cm metal box, the end was lit with the writer, the length with which separator paper burned was measured, and the case where combustion length was less than 1cm was estimated that there is self-extinguishing.

[0056] A result is shown in Table 1.

[0057]

[Example 2] In the example 1, the charge-and-discharge efficiency of a cell and the self-extinguishing of nonaqueous electrolyte were evaluated like the example 1 except having made the addition of vinylene carbonate into 0.5 % of the weight.

[0058] A result is shown in Table 1 and drawing 3.

[0059]

[Example 3] In the example 1, the charge-and-discharge efficiency of a cell and the self-extinguishing of nonaqueous electrolyte were evaluated like the example 1 except having used 4 and 5-dimethyl vinylene carbonate, and having made the addition into 0.5 % of the weight instead of vinylene carbonate.

[0060] A result is shown in Table 1.

[0061]

[Example 4] After dissolving LiPF₆15.2g (100mmol) in the mixed solvent (mixture product ratio EC:DMC:TMPA=

33.95:63.05:3.0) of ethylene carbonate (EC), dimethyl carbonate (DMC), and trimethyl phosphate (TMPA), it added so that the vinylene carbonate concentration in nonaqueous electrolyte might become 0.5 % of the weight, and nonaqueous electrolyte was prepared (electrolyte concentration of 1.0 mols/l.). The charge-and-discharge efficiency of a cell and the self-extinguishing of nonaqueous electrolyte were evaluated like the example 1 using the obtained nonaqueous electrolyte.

[0062] A result is shown in Table 1 and drawing 3.

[0063]

[Example 5] About LiPF₆15.2g (100mmol), it is the mixed solvent (it was referred to as mixed volume-ratio EC:DMC:TMPA=32.55:60.45:7.0, it added so that the vinylene carbonate concentration in nonaqueous electrolyte might become 0.5 % of the weight, and nonaqueous electrolyte was prepared (electrolyte concentration of 1.0 mols/l.)) of ethylene carbonate (EC), dimethyl carbonate (DMC), and trimethyl phosphate (TMPA). The charge-and-discharge efficiency of a cell and the self-extinguishing of nonaqueous electrolyte were evaluated like the example 1 using the obtained nonaqueous electrolyte.

[0064] A result is shown in Table 1 and drawing 3.

[0065]

[Table 1]

表 1

	非水溶媒組成 (体積比)			ビニレンカーボネート添加量(重量%)	充放電効率 %	自己消火性
	EC	DMC	TMPA			
実施例 1	33.25	61.75	5.0	0.1	91.9	あり
実施例 2	33.25	61.75	5.0	0.5	94.1	あり
実施例 3	33.25	61.75	5.0	0.5	92.2	あり
実施例 4	33.95	63.05	3.0	0.5	94.9	あり
実施例 5	32.55	60.45	7.0	0.5	91.7	あり

* 実施例3では、4,5-ジメチルビニレンカーボネートを使用した。

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TECHNICAL FIELD

[Field of the Invention] this invention relates to the nonaqueous electrolyte rechargeable battery containing this electrolytic solution while relating to the nonaqueous electrolyte which it is still more detailed, and fire retardancy is high, was safe, and could generate the high voltage, and was excellent in cell charge/discharge capability ability about nonaqueous electrolyte and a nonaqueous electrolyte rechargeable battery.

[0002]

Background of the Invention] Nonaqueous electrolyte is used as the electrolytic solution of energy-storage devices, such as a lithium cell and an electric double layer capacitor, and since these devices have a high voltage and high-energy density and are excellent in reliability, they are widely used for the power supply of consumer electronics etc. Nonaqueous electrolyte consists of a non-aqueous solvent and an electrolyte, and propylene carbonate [which is generally the organic solvent of a high dielectric constant], gamma-butyrolactone, sulfolane or dimethyl carbonate that is the organic solvent of hypoviscosity], dimethoxyethane, tetrahydrofuran, 1, and 3-dioxolane etc. is used as a non-aqueous solvent. Moreover, as an electrolyte, Et4NBF4, LiBF4, LiPF6, LiClO4 and LiAsF6, LiCF3SO3, LiAlCl4, LiSiF6, etc. are used.

[0003] By the way, since a cell with a high energy density is desired, research is advanced about the high-voltage cell. For example, the rechargeable battery called rocking-chair type which used the lithium of LiCoO2, LiNiO2, and LiMn2O4 grade and the multiple oxide of transition metals for the positive electrode of a cell, and used the carbon material for the negative electrode is studied. since [in this case,] a cell voltage can generate more than 4V and moreover does not have a deposit of a metal lithium — overcharge and external short-circuit — ****(ing) — crushing — etc. — also by experiment, it is checked that safety is secured and it appears on the market as a noncommercial use. However, when the future large formation of high-energy density and enlargement are made, to raise safety further is desired and it is called for that inflammable nonaqueous electrolyte has self-extinguishing.

[0004] For this reason, adding the phosphoric ester known as a compound with self-extinguishing to the electrolytic solution is proposed (for example, refer to JP,4-184870,A).

[0005] However, although the electrolytic solution which added general phosphoric ester, such as phosphoric-acid triethyl, is fire retardancy and safety improved, depending on the kind and addition of phosphoric ester, there were also cell charge-and-discharge efficiency, an energy density of a cell, and a thing that cannot necessarily be satisfied in respect of a battery life.

[0006]

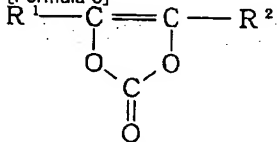
[Objects of the Invention] this invention aims at offering the rechargeable battery containing this nonaqueous electrolyte while it aims at offering the nonaqueous electrolyte which was made in view of the above-mentioned trouble, fire retardancy was highly safe, and could generate the high voltage, and was excellent in cell charge/discharge capability ability.

[0007]

[Summary of the Invention] The nonaqueous electrolyte concerning this invention is characterized by the bird clapper from the non-aqueous solvent containing the vinylene carbonate derivative expressed with the following general formula [I], and a phosphoric ester compound, and the electrolyte.

[0008]

[Formula 3]

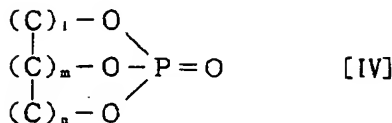
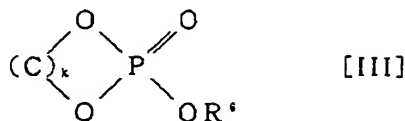
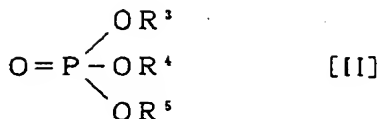


[I]

[0009] (Among a formula, even if R1 and R2 are mutually the same, they may differ from each other, and they show a hydrogen atom or the alkyl group of carbon numbers 1-3.)

It is desirable that the aforementioned phosphoric ester compound is phosphoric ester expressed with following general formula [II] - [IV], and it is [0010].

[Formula 4]



[0011] (Among a formula, even if R3-R6 are mutually the same, they may differ from each other, and they show the alkyl group or fluorine substitution alkyl group of carbon numbers 1-6.) - (C)- is the hydrocarbon group of the shape of a straight chain, and the letter of branching, k, l, m, and n show a carbon number, k is the integer of 2-8, and at least one of l, m, and the n is [it may differ, even if l, m, and n are mutually the same, and it is the integer of 0-12, and] one or more integers. It is desirable especially that it is trimethyl phosphate.

[0012] As for the aforementioned non-aqueous solvent, it is desirable that at least one sort of an annular carbonate and a chain-like carbonate is included further. The nonaqueous electrolyte rechargeable battery concerning this invention is characterized by the lithium, the positive electrode containing the multiple oxide of transition metals, and having the aforementioned nonaqueous electrolyte as the electrolytic solution as the negative electrode which contains a metal lithium, a lithium content alloy, or the carbon material in which the dope and ** dope of a lithium ion are possible as a negative-electrode active material, and a positive active material.

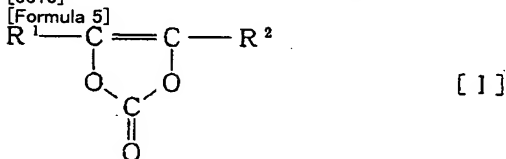
[0013]

[Detailed Description of the Invention] Hereafter, the nonaqueous electrolyte concerning this invention and the nonaqueous electrolyte rechargeable battery using this nonaqueous electrolyte are explained concretely.

[0014] The nonaqueous electrolyte concerning this invention consists of a non-aqueous solvent containing a specific vinylene carbonate derivative and a specific phosphoric ester compound, and an electrolyte.

What is expressed with the following general formula [I] as a vinylene carbonate derivative used by the vinylene carbonate derivative this invention is used.

[0015]



[0016] (Among a formula, even if R1 and R2 are mutually the same, they may differ from each other, and they show a hydrogen atom or the alkyl group of carbon numbers 1-3.)

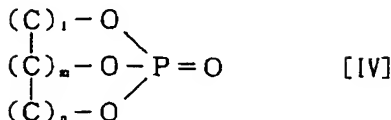
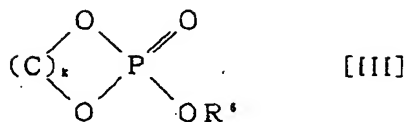
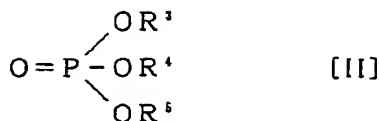
As such a vinylene carbonate derivative, vinylene carbonate, 4, 5-dimethyl vinylene carbonate, 4, 5-diethyl vinylene carbonate, 4, 5-dipropyl vinylene carbonate, 4-ethyl-5-methyl vinylene carbonate, 4-ethyl-5-propyl vinylene carbonate, 4-methyl-5-propyl vinylene carbonate, etc. are mentioned.

[0017] There is an effect of improving the charge-and-discharge efficiency of the cell produced in case a phosphoric ester compound is added, and the fall of a load characteristic in such a vinylene carbonate derivative.

As a phosphoric ester compound used by the phosphoric ester compound this invention, the phosphoric ester expressed with following general formula [II] - [IV] is used preferably.

[0018]

[Formula 6]



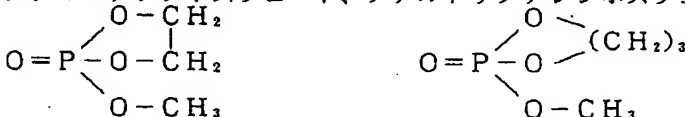
[0019] (Among a formula, even if R3-R6 are mutually the same, they may differ from each other, and they show the alkyl group or fluorine substitution alkyl group of carbon numbers 1-6.) - (C)- is the hydrocarbon group of the shape of a straight chain, and the letter of branching, k, l, m, and n show a carbon number, k is the integer of 2-8, and at least one of l, m, and the n is [it may differ, even if l, m, and n are mutually the same, and it is the integer of 0-12, and] one or more integers.

Specifically as phosphoric ester expressed with a formula [II], trimethyl phosphate, triethyl phosphate, TORIPURO pill phosphate, tributyl phosphate, dimethyl ethyl phosphate, methyl diethyl phosphate, etc. are mentioned.

[0020] Specifically as phosphoric ester expressed with a formula [III], it is [0021].

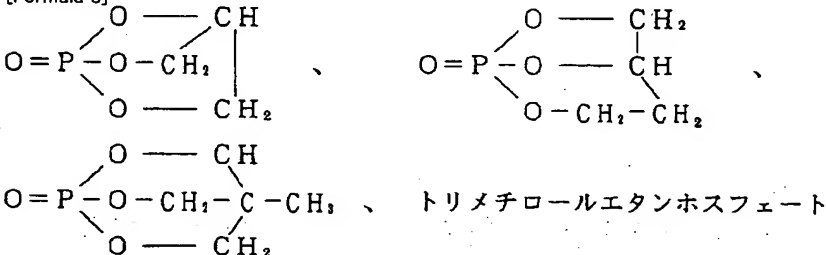
[Formula 7]

メチルエチレンホスフェート、メチルトリメチレンホスフェート



[0022] **** is mentioned. Specifically as phosphoric ester expressed with a formula [IV], it is [0023].

[Formula 8]



[0024] **** is mentioned. In respect of fire-resistant grant, since the effect is large, trimethyl phosphate and phosphoric-acid triethyl are desirable, and especially trimethyl phosphate is [among these] desirable.

[0025] In the nonaqueous electrolyte concerning a non-aqueous-solvent this invention, the non-aqueous solvent containing the above vinylene carbonate derivatives and a phosphoric ester compound is used.

[0026] As for the aforementioned phosphoric ester compound, it is preferably desirable one to 40 volume % and to be contained in the amount of 3 - 25 volume % still more preferably in a non-aqueous solvent more than 0.1 volume %. If the phosphoric ester compound is contained in the non-aqueous solvent in such an amount, sufficient fire retardancy for nonaqueous electrolyte can be given.

[0027] Moreover, the non-aqueous-solvent pair of the aforementioned vinylene carbonate derivative is carried out, and it is preferably desirable to be added in 0.1 - 5% of the weight of the amount still more preferably 0.01 to 20% of the weight 0.001% of the weight or more. The charge-and-discharge efficiency of the cell produced in case a phosphoric ester compound will be added, if the vinylene carbonate derivative is added in the non-aqueous solvent in such an amount, and the fall of a load characteristic are fully improvable.

[0028] It is desirable to contain carbonates, such as an annular carbonate and chain-like carbonate, in the non-aqueous solvent used by this invention in addition to a vinylene carbonate derivative and a phosphoric ester compound. By including such a carbonate, the charge-and-discharge efficiency and the load characteristic of a cell are further improvable.

[0029] As an annular carbonate, ethylene carbonate, propylene carbonate, butylene carbonate, etc. are mentioned. these — one sort — or two or more sorts may use it, mixing The mixed solvent of ethylene carbonate, propylene carbonate or ethylene carbonate, and propylene carbonate is preferably used among these annular carbonates. If the

annular carbonate is contained, it is possible to raise the solubility of the electrolyte in low temperature, transportation of an electrolyte can become easy, and the electrical conductivity of the electrolytic solution can be raised further.

[0030] As a chain-like carbonate, dimethyl carbonate, methylethyl carbonate, diethyl carbonate, methylpropyl carbonate, methyl isopropyl carbonate, ethyl propyl carbonate, etc. are mentioned, these — one sort — or two or more sorts may be used, mixing. Since dimethyl carbonate can raise the self-extinguishing of the electrolytic solution among these chain-like carbonates, it is desirable. If these chain-like carbonates are contained in the non-aqueous solvent, it is possible to make viscosity of nonaqueous electrolyte low, and electrolytic solubility can be raised further and it can consider as the electrolytic solution excellent in the electrical conductivity in ordinary temperature or low temperature.

[0031] The above chain-like carbonates and annular carbonates can also be mixed and used, such a carbonate — the non-aqueous-solvent whole quantity — receiving — ten to 99 volume % — it is preferably desirable 40 to 97 volume % and to be contained in the amount of 80 — 97 volume % still more preferably.

[0032] If it is possible to raise the electrical conductivity of nonaqueous electrolyte if the annular carbonate is contained in the non-aqueous solvent in such an amount and the chain-like carbonate is contained, nonaqueous electrolyte excellent in self-extinguishing can be obtained.

[0033] In the non-aqueous solvent used by this invention further again, the above-mentioned phosphoric ester, a vinylene carbonate derivative, The methyl formate usually used as a non-aqueous solvent for cells besides an annular carbonate and chain-like carbonate, An ethyl formate, a propyl formate, methyl acetate, ethyl acetate, propyl acetate, Chain-like ether, such as chain-like ester, such as a methyl propionate and an ethyl propionate, and dimethoxyethane, Amides, such as cyclic ether, such as a tetrahydrofuran, and a dimethylformamide Methyl — Chain-like carver mates, such as N and N-dimethyl carver mate Annular sulfones, such as cyclic ester, such as gamma-butyrolactone, and a sulfolane Non-aqueous solvents, such as annular ureas, such as cyclic-amides [such as annular carver mates, such as N-methyl oxazolidinone and N-methyl pyrrolidone,], N, and N-dimethyl imidazolidone, etc. can be used.

[0034] As an electrolyte which is dissolving into electrolyte nonaqueous electrolyte For example LiPF₆, LiBF₄, LiClO₄, LiAsF₆, LiCF₃SO₃, LiN(SO₂CF₃)₂, LiN(SO₂C₂F₅)₂, LiC(SO₂CF₃)₃, LiN(SO₃CF₃)₂, LiN(SO₃CH₂CF₃)₂, LiAlCl₄, LiSiF₆, Lithium salt, such as LiC₄F₉SO₃ and LiC₈F₁₇SO₃, is mentioned. These lithium salt may be used independently, and may mix and use two or more sorts of lithium salt.

[0035] Since LiPF₆ and LiBF₄ become [fire retardancy] high by the synergism with phosphoric ester among these lithium salt, it is used preferably. As for such an electrolyte, it is usually desirable to contain 0.1–3 mols /in nonaqueous electrolyte by the concentration of 0.5–2 mols/l. preferably l.

[0036] The nonaqueous electrolyte rechargeable battery concerning a nonaqueous electrolyte rechargeable battery this invention consists of a lithium, a positive electrode containing the multiple oxide of transition metals, and aforementioned nonaqueous electrolyte as the negative electrode which contains a metal lithium, a lithium content alloy, or the carbon material in which the dope and ** dope of a lithium ion are possible as a negative-electrode active material, and a positive active material.

[0037] Such a nonaqueous electrolyte rechargeable battery is applicable to for example, a cylindrical nonaqueous electrolyte rechargeable battery. It comes to contain a cylindrical nonaqueous electrolyte rechargeable battery with the cell can 5, where an electric insulating plate 4 is laid in the upper and lower sides of winding and a winding object through the separator 3 into which nonaqueous electrolyte was poured for the negative electrode 1 which applies a negative-electrode active material to the negative-electrode charge collector 9, and becomes it as shown in drawing 1, and the positive electrode 2 which comes to apply a positive active material to the positive-electrode charge collector 10, the cell can 5 — the cell lid 7 — the obturation gasket 6 — minding — by closing, it is attached and connects with a negative electrode 1 or a positive electrode 2 electrically through the negative-electrode lead 11 and the positive-electrode lead 12, respectively, and it is constituted so that it may function as the negative electrode or positive electrode of a cell in addition, separator is a porous film.

[0038] By this cell, as for the positive-electrode lead 12, electrical installation with the cell lid 7 may be measured through the sheet metal 8 for current interception. By such cell, if the pressure inside a cell rises, the sheet metal 8 for current interception is pushed up, and deforms, the positive-electrode lead 12 leaves the above-mentioned sheet metal 8 and the welded portion, and is cut, and current has become as [intercept / current].

[0039] Although any of the carbon material as a negative-electrode active material which constitutes such a negative electrode 1 which can dope and ** dope a metal lithium, a lithium alloy, and a lithium ion can be used, it is desirable to use the carbon material which can dope and ** dope a lithium ion among these. Such a carbon material may be an amorphous carbon even if it is graphite, and all carbon materials, such as activated carbon, a carbon fiber, carbon black, and a meso carbon micro bead, are used.

[0040] Especially in this invention, the spacing (d002) of the field (002) measured with X-ray analysis is 0.37nm or less, and if the carbon material which has a property near the graphite whose density is three or more 1.70 g/cm³ is desirable and uses such a carbon material, the energy density of a cell can be made high.

[0041] Moreover, the multiple oxide which the multiple oxide which consists of the lithium and transition metals of transition-metals oxides, such as MoS₂, TiS₂, MnO₂, and V₂O₅, and a transition-metals sulfide or LiCoO₂ and LiMnO₂, LiMn₂O₄, and LiNiO₂ grade is used as a positive active material which constitutes a positive electrode 2, and especially consists of a lithium and transition metals is desirable.

[0042] Moreover, the nonaqueous electrolyte rechargeable battery concerning this invention is applicable also to a coin type nonaqueous electrolyte rechargeable battery as shown in drawing 2. with the coin type nonaqueous electrolyte rechargeable battery of drawing 2, the disk-like negative electrode 13, the disk-like positive electrode 14, separator 15, and the stainless board 17 contain with the cell can 16, where a laminating is carried out in the sequence of the stainless board 17, a negative electrode 13, separator 15, a positive electrode 14, and — having — the cell can (lid) 19 — a gasket 18 — minding — it is attached by closing The same thing as the above is used as a negative electrode 13, separator 15, and a positive electrode 14. Moreover, the thing of the quality of the material of the stainless steel which cannot corrode the cell can 16 and the cell can (lid) 19 easily due to the electrolytic solution is used.

[0043] In addition, it may not be limited to what showed the configuration of a cell etc. to drawing 1 and drawing 2 including the nonaqueous electrolyte which explained the nonaqueous electrolyte rechargeable battery concerning this invention above as the electrolytic solution, but you may be a square shape etc.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] The nonaqueous electrolyte concerning this invention is fire retardancy, and excellent in charge/discharge capability ability, and the nonaqueous electrolyte rechargeable battery using such nonaqueous electrolyte is safe, can generate the high voltage, and is excellent in a charge-and-discharge property.

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EXAMPLE

[Example] Although an example is given and this invention is explained concretely hereafter, this invention is not limited at all by these examples.

[0046]

[Example 1] After dissolving <manufacture of nonaqueous electrolyte> LiPF₆ 15.2g (100mmol) in the mixed solvent (mixture product ratio EC:DMC:TMPA= 33.25:61.75:5.0) of ethylene carbonate (EC), dimethyl carbonate (DMC), and trimethyl phosphate (TMPA), it added so that the vinylene carbonate concentration in nonaqueous electrolyte might become 0.1 % of the weight, and nonaqueous electrolyte was prepared (electrolyte concentration of 1.0 mols/l.).

[0047] <production of a negative electrode> — the negative electrode 13 was produced as follows first 95 weight sections and the polyvinylidene-fluoride (PVDF) 5 weight section of a binder are mixed in the carbon-powder end of the mezzo-soprano phase PITCHIMAKUIRO fiber made from PETOKA (tradename : mel BUROMMIRUDO, d 002= 0.336nm, density 2.21 g/cm³), and it distributes to N-methyl pyrrolidone of a solvent — making — a negative electrode — a mixture — the slurry (the shape of a paste) was prepared

[0048] this negative electrode — a mixture — the slurry was applied to the negative-electrode charge collector with a thickness of 20 micrometers made from band-like copper foil, and the dried band-like carbon electrode was obtained such a carbon electrode — the thickness of a mixture was 25 micrometers After piercing this band electrode with a diameter of 15mm in the shape of a disk furthermore, it pressed and considered as the negative electrode 13.

[0049] The <production of positive electrode> positive electrode 14 was produced as follows. the LiCoO₂ (21 8 micrometers of mean particle diameters [Product name : HLC-]) 91 weight section by Honjo Chemical, the graphite 6 weight section of electric conduction material, and the polyvinylidene-fluoride 3 weight section of a binder — mixing — a positive electrode — preparing a mixture and distributing N-methyl pyrrolidone — a positive electrode — a mixture — the slurry was obtained

[0050] The positive-electrode charge collector made from a band-like aluminum foil with a thickness of 20 micrometers was made to apply and dry this slurry, it pressed, and the band-like positive electrode was obtained.

***** of such a positive electrode was 40 micrometers. It considered as the positive-electrode electrode 14 by furthermore piercing this band electrode with a diameter of 15mm in the shape of a disk.

[0051] <production of a cell> — as shown in drawing 2, after carrying out the laminating of the disk-like negative electrode 13 obtained by doing in this way, the disk-like positive electrode 14, and the separator 15 (micrometers [in thickness / 25], fine porosity polypropylene film with a diameter of 19mm) to the cell can 16 of 2032 sizes made from stainless steel in the sequence of a negative electrode 13, separator 15, and a positive electrode 14, the aforementioned nonaqueous electrolyte was poured into separator 15 Then, after containing the board 17 (the thickness of 2.4mm, diameter of 15.4mm) made from stainless steel, through the gasket 18 made from polypropylene, by closing the cell can (lid) 19, the airtightness in a cell was held and the button type nonaqueous electrolyte rechargeable battery with a diameter [of 20mm] and a height of 3.2mm was produced.

[0052] <measurement of service capacity and a load characteristic> — the service capacity of the nonaqueous electrolyte rechargeable battery which carried out in this way and was produced was measured In addition, in this example, the direction of current where Li⁺ is doped by the negative electrode was considered as charge, and the direction of current by which a ** dope is carried out was considered as charge.

[0053] Charge was performed by the 4.2V or 1mA constant-current constant-voltage method, and when the charging current became below 50microA, it considered as the end. Electric discharge was performed by the 1mA constant current, and when voltage amounted to 2.7V, it considered as the end. From the charge capacity of this charge-and-discharge cycle, and service capacity, charge-and-discharge efficiency was measured by the following formula. A result is shown in Table 1.

[0054]

[Equation 1]

$$\text{充放電効率 (\%)} = \frac{\text{放電容量 (mAh/g)}}{\text{充電容量 (mAh/g)}} \times 100$$

[0055] The Manila paper for separators with a thickness of 0.04mm cut with a length of 30cm 15mm and in the shape of a strip of paper in the beaker containing the <self-extinguishing evaluation of nonaqueous electrolyte> aforementioned nonaqueous electrolyte was dipped 1 minute or more. The superfluous nonaqueous electrolyte which drips from Manila paper was wiped with the beaker wall, the support needle of the sample base which has a support needle at intervals of 2.5cm was stabbed with Manila paper, and it fixed horizontally. The sample base which fixed Manila paper was put into the 25cmx25cmx50cm metal box, the end was lit with the writer, the length with which separator paper burned was measured, and the case where combustion length was less than 1cm was estimated that there is self-extinguishing.

[0056] A result is shown in Table 1.

[0057]

[Example 2] In the example 1, the charge-and-discharge efficiency of a cell and the self-extinguishing of nonaqueous electrolyte were evaluated like the example 1 except having made the addition of vinylene carbonate into 0.5 % of the weight.

[0058] A result is shown in Table 1 and drawing 3.

[0059]

[Example 3] In the example 1, the charge-and-discharge efficiency of a cell and the self-extinguishing of nonaqueous electrolyte were evaluated like the example 1 except having used 4 and 5-dimethyl vinylene carbonate, and having made the addition into 0.5 % of the weight instead of vinylene carbonate.

[0060] A result is shown in Table 1.

[0061]

[Example 4] After dissolving LiPF₆15.2g (100mmol) in the mixed solvent (mixture product ratio EC:DMC:TMPA=33.95:63.05:3.0) of ethylene carbonate (EC), dimethyl carbonate (DMC), and trimethyl phosphate (TMPA), it added so that the vinylene carbonate concentration in nonaqueous electrolyte might become 0.5 % of the weight, and nonaqueous electrolyte was prepared (electrolyte concentration of 1.0 mols/l.). The charge-and-discharge efficiency of a cell and the self-extinguishing of nonaqueous electrolyte were evaluated like the example 1 using the obtained nonaqueous electrolyte.

[0062] A result is shown in Table 1 and drawing 3.

[0063]

[Example 5] About LiPF₆15.2g (100mmol), it is the mixed solvent (it was referred to as mixed volume-ratio EC:DMC:TMPA=32.55:60.45:7.0, it added so that the vinylene carbonate concentration in nonaqueous electrolyte might become 0.5 % of the weight, and nonaqueous electrolyte was prepared (electrolyte concentration of 1.0 mols/l.).) of ethylene carbonate (EC), dimethyl carbonate (DMC), and trimethyl phosphate (TMPA). The charge-and-discharge efficiency of a cell and the self-extinguishing of nonaqueous electrolyte were evaluated like the example 1 using the obtained nonaqueous electrolyte.

[0064] A result is shown in Table 1 and drawing 3.

[0065]

[Table 1]

表 1

	非水溶媒組成 (体積比)			ビニレンカーボネート添加量 (重量%)	充放電効率 %	自己消火性
	EC	DMC	TMPA			
実施例 1	33.25	61.75	5.0	0.1	91.9	あり
実施例 2	33.25	61.75	5.0	0.5	94.1	あり
実施例 3	33.25	61.75	5.0	0.5	92.2	あり
実施例 4	33.95	63.05	3.0	0.5	94.9	あり
実施例 5	32.55	60.45	7.0	0.5	91.7	あり

* 実施例3では、4, 5-ジメチルビニレンカーボネートを使用した。

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the outline cross section of the cylindrical cell in which one example of the nonaqueous electrolyte rechargeable battery of this invention is shown.

[Drawing 2] It is the outline cross section of the coin cell in which one example of the nonaqueous electrolyte rechargeable battery of this invention is shown.

[Drawing 3] It is drawing showing the change of charge-and-discharge efficiency to TMPA in the example and the example of comparison of this invention.

[Description of Notations]

- 1 13 Negative electrode
- 2 14 Positive electrode
- 3 15 Separator
- 4 Electric insulating plate
- 5 16 Cell can
- 6 Obturation gasket
- 7 Cell lid
- 8 Sheet metal for current interception
- 9 Negative-electrode charge collector
- 10 Positive-electrode charge collector
- 11 Negative-electrode lead
- 12 Positive-electrode lead
- 17 Board made from stainless steel
- 18 Gasket
- 19 Cell can (lid)

[Translation done.]

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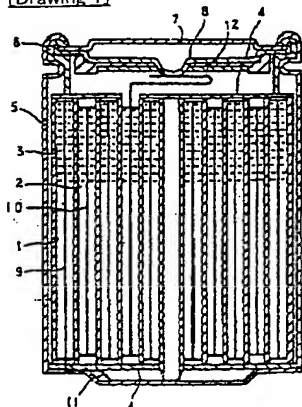
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2.*** shows the word which can not be translated.

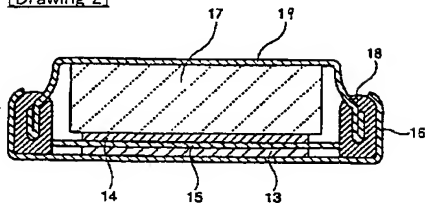
3.In the drawings, any words are not translated.

DRAWINGS

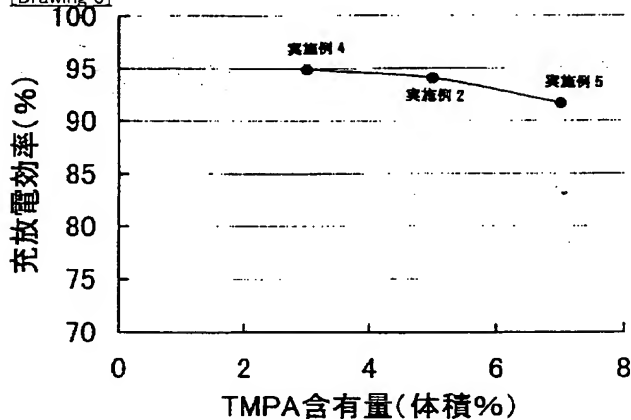
[Drawing 1]



[Drawing 2]



[Drawing 3]



[Translation done.]

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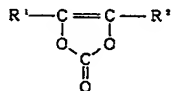
(54) 【発明の名称】 非水電解液及び非水電解液二次電池

(57) 【要約】

【課題】 難燃性が高く安全で、高電圧を発生でき、かつ電池充放電性能の優れた非水電解液を提供する。

【解決手段】 下記一般式〔I〕で表されるビニレンカーボネート誘導体とリン酸エステル化合物とを含む非水溶媒と、電解質とからなることを特徴とする非水電解液。

【化1】



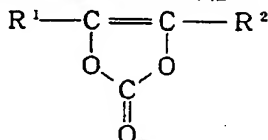
〔I〕

(式中、R¹およびR²は互いに同一であっても異なってもよく、水素原子または炭素数1～3のアルキル基を示す。)

(2)

【特許請求の範囲】

【請求項1】下記一般式〔I〕で表されるビニレンカーボネート誘導体とリン酸エステル化合物とを含む非水溶液*

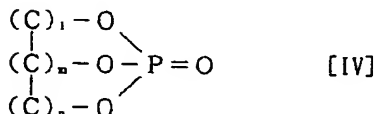
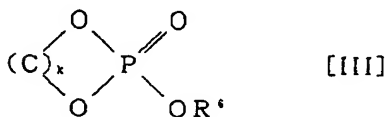
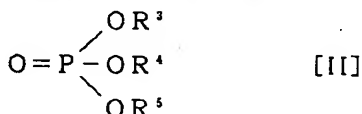


〔I〕

(式中、 R^1 および R^2 は互いに同一であっても異なってもよく、水素原子または炭素数1～3のアルキル基を示す。)

【請求項2】前記リン酸エステル化合物が、下記一般式〔II〕～〔IV〕で表されるリン酸エステルであることを特徴とする請求項1に記載の非水電解液。

〔化2〕



(式中、 $\text{R}^3 \sim \text{R}^6$ は互いに同一であっても異なってもよく、炭素数1～6のアルキル基またはフッ素置換アルキル基を示す。-(C)-は、直鎖状または分岐状の炭化水素基であり、k、l、m、nは炭素数を示し、kは2～8の整数であり、l、m、nは互いに同一であっても異なってもよく0～12の整数であり、l、m、nの少なくとも1つは1以上の整数である。)

【請求項3】前記リン酸エステル化合物が、リン酸トリメチルであることを特徴とする請求項1または2に記載の非水電解液。

【請求項4】前記非水溶媒が、環状炭酸エステルおよび鎖状炭酸エステルから選ばれる少なくとも1種の炭酸エステルをさらに含むことを特徴とする請求項1～3のいずれかに記載の非水電解液。

【請求項5】負極活物質として金属リチウム、リチウム含有合金、リチウムイオンのドーブ・脱ドーブが可能な炭素材料のいずれかを含む負極と、正極活物質としてリチウムと遷移金属の複合酸化物を含む正極と、

電解液として請求項1～4のいずれかに記載の非水電解

* 媒と、

電解質とからなることを特徴とする非水電解液。

〔化1〕

液とを、

有することを特徴とする非水電解液二次電池。

【発明の詳細な説明】

【0001】

【発明の技術分野】本発明は、非水電解液および非水電解液二次電池に関し、さらに詳しくは難燃性が高く安全で、高電圧を発生でき、かつ電池充放電性能の優れた非水電解液に関するとともに、この電解液を含む非水電解液二次電池に関する。

【0002】

【発明の技術的背景】非水電解液は、リチウム電池や電気二重層コンデンサなどエネルギー貯蔵デバイスの電解液として使用され、これらのデバイスは高電圧、高エネルギー密度を有し、信頼性に優れているため、広く民生用電子機器の電源などに用いられている。非水電解液は、非水溶媒と電解質とからなり、非水溶媒としては、一般に高誘電率の有機溶媒であるプロピレンカーボネート、γ-ブチロラクトン、スルホラン、あるいは低粘度の有機溶媒であるジメチルカーボネート、ジメトキシエタン、テトラヒドロフラン、1,3-ジオキソランなどが用いられている。また電解質としては、 Et_4NBF_4 、 LiBF_4 、 LiPF_6 、 LiClO_4 、 LiAsF_6 、 LiCF_3SO_3 、 LiAlCl_4 、 LiSiF_6 などが用いられている。

【0003】ところで、エネルギー密度の高い電池が望まれていることから、高電圧電池について研究が進められている。例えば、電池の正極に LiCoO_2 、 LiNiO_2 、 LiMn_2O_4 等のリチウムと遷移金属の複合酸化物を使用し、負極に炭素材料を使用した、ロッキングチェア型と呼ばれる二次電池が研究されている。この場合、電池電圧は4V以上を発生することができ、しかも金属リチウムの析出がないため、過充電、外部ショート、釘刺し、押しつぶし等の実験によっても安全性が確保されることが確認され、民生用として出回るようになっていく。しかしながら、今後の大幅な高エネルギー密度化、また、大型化がなされた場合には、さらに安全性を向上させることが望まれ、可燃性の非水電解液は自己消火性を有することが求められている。

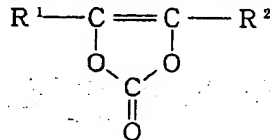
【0004】このため、自己消火性のある化合物として知られているリン酸エステル類を電解液に添加することが提案されている(たとえば特開平4-184870号公報参照)。

(3)

【0005】しかしながら、リン酸トリエチルなどの一般的なリン酸エステル類を添加した電解液は、難燃性であって安全性は向上されるが、リン酸エステルの種類や添加量によっては、電池充放電効率、電池のエネルギー密度、電池寿命の点で必ずしも満足できないものもあった。

【0006】

【発明の目的】本発明は、上記の問題点に鑑みなされたもので、難燃性が高く安全で、高電圧を発生でき、かつ電池充放電性能の優れた非水電解液を提供することを目的とする。



[I]

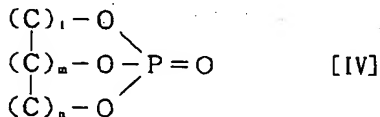
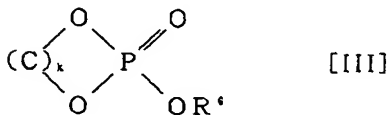
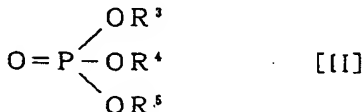
【0009】(式中、 R^1 および R^2 は互いに同一であっても異なってもよく、水素原子または炭素数1~3のアルキル基を示す。)

前記リン酸エステル化合物が、下記一般式【II】~【I

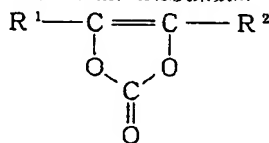
V】で表されるリン酸エステルであることが好ましく、

【0010】

【化4】



【0011】(式中、 $\text{R}^3 \sim \text{R}^6$ は互いに同一であっても異なってもよく、炭素数1~6のアルキル基またはフッ素置換アルキル基を示す。-(C)-は、直鎖状または分岐状の炭化水素基であり、k、l、m、nは炭素数※



[I]

【0016】(式中、 R^1 および R^2 は互いに同一であっても異なってもよく、水素原子または炭素数1~3のアルキル基を示す。)

※的とするとともに、この非水電解液を含む二次電池を提供することを目的としている。

【0007】

【発明の概要】本発明に係る非水電解液は、下記一般式【I】で表されるビニレンカーボネート誘導体とリン酸エステル化合物とを含む非水溶媒と、電解質とからなることを特徴としている。

【0008】

【化3】

※を示し、kは2~8の整数であり、l、m、nは互いに同一であっても異なってもよく0~12の整数であり、l、m、nの少なくとも1つは1以上の整数である。特に、リン酸トリメチルであることが好ましい。

【0012】前記非水溶媒は、さらに環状炭酸エステルと鎖状炭酸エステルの少なくとも1種を含むことが好ましい。本発明に係る非水電解液二次電池は、負極活物質として金属リチウム、リチウム含有合金、リチウムイオンのドーブ・脱ドーブが可能な炭素材料のいずれかを含む負極と、正極活物質としてリチウムと遷移金属の複合酸化物を含む正極と、電解液として前記非水電解液とを、有することを特徴としている。

【0013】

【発明の具体的な説明】以下、本発明に係る非水電解液およびこの非水電解液を用いた非水電解液二次電池について具体的に説明する。

【0014】本発明に係る非水電解液は、特定のビニレンカーボネート誘導体とリン酸エステル化合物とを含む非水溶媒と、電解質とからなる。

ビニレンカーボネート誘導体

本発明で用いられるビニレンカーボネート誘導体としては下記一般式【I】で表されるものが使用される。

【0015】

【化5】

このようなビニレンカーボネート誘導体としては、ビニレンカーボネート、4,5-ジメチルビニレンカーボネート、4,5-ジエチルビニレンカーボネート、4,5-ジプロピ

(4)

ルビニレンカーボネート、4-エチル-5-メチルビニレンカーボネート、4-エチル-5-プロピルビニレンカーボネート、4-メチル-5-プロピルビニレンカーボネートなどが挙げられる。

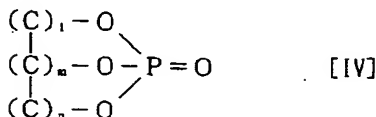
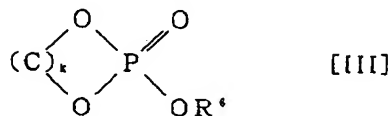
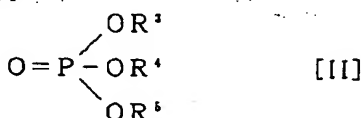
【0017】このようなビニレンカーボネート誘導体には、リン酸エステル化合物を添加する際に生じる電池の充放電効率および負荷特性の低下を改善する効果がある。

リン酸エステル化合物

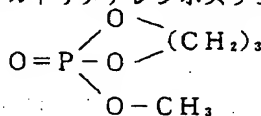
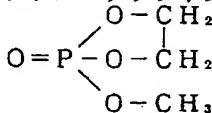
本発明で用いられるリン酸エステル化合物として、下記一般式 [II] ~ [IV] で表されるリン酸エステルが好ましく使用される。

【0018】

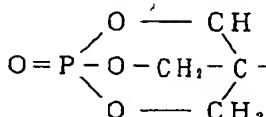
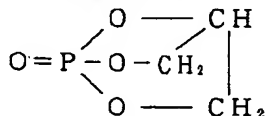
【化6】



メチルエチレンホスフェート、メチルトリメチレンホスフェート

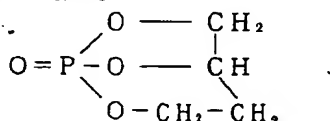


【0022】などが挙げられる。式 [IV] で表されるリン酸エステルとして、具体的には、



* 【0023】

【化8】



トリメチロールエタンホスフェート

【0024】などが挙げられる。これらのうち、リン酸トリメチル、リン酸トリエチルが難燃性付与の点で効果が大きいので好ましく、とくにリン酸トリメチルが好ましい。

【0019】(式中、 $\text{R}^3 \sim \text{R}^6$ は互いに同一であっても異なってもよく、炭素数1~6のアルキル基またはフッ素置換アルキル基を示す。-(C)-は、直鎖状または分岐状の炭化水素基であり、k、l、m、nは炭素数を示し、kは2~8の整数であり、l、m、nは互いに同一であっても異なってもよく0~12の整数であり、l、m、nの少なくとも1つは1以上の整数である。)

式 [II] で表されるリン酸エステルとして、具体的には、トリメチルホスフェート、トリエチルホスフェート、トリプロピルホスフェート、トリブチルホスフェート、ジメチルエチルホスフェート、メチルジエチルホスフェートなどが挙げられる。

【0020】式 [III] で表されるリン酸エステルとして、具体的には、

【0021】

【化7】

【0025】非水溶媒

本発明に係る非水電解液では、上記のようなビニレンカーボネート誘導体とリン酸エステル化合物とを含む非水溶媒が使用される。

(5)

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【0026】前記リン酸エステル化合物は、非水溶媒中に、0.1体積%以上、好ましくは1~40体積%、さらに好ましくは3~25体積%の量で含まれていることが望ましい。このような量で非水溶媒中にリン酸エステル化合物が含まれていると、非水電解液に十分な難燃性を付与することができる。

【0027】また、前記ビニレンカーボネート誘導体は、非水溶媒対して、0.001重量%以上、好ましくは0.01~20重量%、さらに好ましくは0.1~5重量%の量で添加されていることが望ましい。このような量で非水溶媒中にビニレンカーボネート誘導体が添加されていると、リン酸エステル化合物を添加する際に生じる電池の充放電効率および負荷特性の低下を十分に改善することができる。

【0028】本発明で用いられる非水溶媒では、ビニレンカーボネート誘導体とリン酸エステル化合物以外に、環状炭酸エステル、鎖状炭酸エステルなどの炭酸エステルが含まれていることが望ましい。このような炭酸エステルを含むことにより、さらに電池の充放電効率および負荷特性を改善することができる。

【0029】環状炭酸エステルとしては、エチレンカーボネート、プロピレンカーボネート、ブチレンカーボネートなどが挙げられる。これらは、1種または2種以上混合して使用してもよい。これらの環状炭酸エステルのうち、エチレンカーボネート、プロピレンカーボネートまたはエチレンカーボネートとプロピレンカーボネートとの混合溶媒が好ましく使用される。環状炭酸エステルが含まれていると、低温における電解質の溶解度を高めることが可能であり、電解質の輸送が容易となり、さらに電解液の電気伝導度を向上させることができる。

【0030】鎖状炭酸エステルとしては、ジメチルカーボネート、メチルエチルカーボネート、ジエチルカーボネート、メチルプロピルカーボネート、メチルイソプロピルカーボネート、エチルプロピルカーボネートなどが挙げられる。これらは、1種または2種以上混合して使用してもよい。これらの鎖状炭酸エステルのうち、ジメチルカーボネートが電解液の自己消火性を高めることができるので好ましい。これらの鎖状炭酸エステルが非水溶媒中に含まれていると、非水電解液の粘度を低くすることが可能であり、電解質の溶解度をさらに高めて、常温または低温での電気伝導性に優れた電解液とすることができる。

【0031】以上のような鎖状炭酸エステルと環状炭酸エステルとは、混合して使用することもできる。このような炭酸エステルは、非水溶媒全量に対して、10~99体積%、好ましくは40~97体積%、さらに好ましくは80~97体積%の量で含まれていることが望ましい。

【0032】このような量で非水溶媒中に環状炭酸エステルが含まれていると、非水電解液の電気伝導度を高め

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ることが可能であり、また鎖状炭酸エステルが含まれていると、自己消火性に優れた非水電解液を得ることができる。

【0033】さらにまた本発明で用いる非水溶媒には、上記リン酸エステル、ビニレンカーボネート誘導体、環状炭酸エステル、鎖状炭酸エステルの他に、通常電池用非水溶媒として用いられる蟻酸メチル、蟻酸エチル、蟻酸プロピル、酢酸メチル、酢酸エチル、酢酸プロピル、プロピオン酸メチル、プロピオン酸エチルなどの鎖状エステル、ジメトキシエタンなどの鎖状エーテル類、テトラヒドロフランなどの環状エーテル類、ジメチルホルムアミドなどのアミド類、メチル-N,N-ジメチルカーバメートなどの鎖状カーバメート類、γ-ブチロラクトンなどの環状エステル、スルホランなどの環状スルホン類、N-メチルオキサソリジノンなどの環状カーバメート、N-メチルピロリドンなどの環状アミド、N,N-ジメチルイミダゾリドンなどの環状ウレア等の非水溶媒などを使用することができる。

【0034】電解質

非水電解液中に溶解している電解質としては、たとえば、 LiPF_6 、 LiBF_4 、 LiClO_4 、 LiAsF_6 、 LiCF_3SO_3 、 $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ 、 $\text{LiN}(\text{SO}_2\text{C}_2\text{F}_5)_2$ 、 $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ 、 $\text{LiN}(\text{SO}_3\text{CF}_3)_2$ 、 $\text{LiN}(\text{SO}_3\text{CH}_2\text{CF}_3)_2$ 、 LiAlCl_4 、 LiSiF_6 、 $\text{LiC}_4\text{F}_9\text{SO}_3$ 、 $\text{LiC}_8\text{F}_{17}\text{SO}_3$ などのリチウム塩が挙げられる。これらのリチウム塩は単独で使用してもよく、2種以上のリチウム塩を混合して使用してもよい。

【0035】これらリチウム塩のうち、 LiPF_6 、 LiBF_4 がリン酸エステルとの相乗作用で難燃性が高くなるため好ましく使用される。このような電解質は、通常、0.1~3モル/リットル、好ましくは0.5~2モル/リットルの濃度で非水電解液に含まれていることが望ましい。

【0036】非水電解液二次電池

本発明に係る非水電解液二次電池は、負極活物質として金属リチウム、リチウム含有合金、リチウムイオンのドーブ・脱ドーブが可能な炭素材料のいずれかを含む負極と、正極活物質としてリチウムと遷移金属の複合酸化物を含む正極と、前記の非水電解液とから構成されている。

【0037】このような非水電解液二次電池は、たとえば円筒型非水電解液二次電池に適用できる。円筒型非水電解液二次電池は、図1に示すように負極集電体9に負極活物質を塗布してなる負極1と、正極集電体10に正極活物質を塗布してなる正極2とを、非水電解液を注入されたセパレータ3を介して巻回し、巻回体の上下に絶縁板4を載置した状態で電池缶5に収納してなるものである。電池缶5には電池蓋7が封口ガasket6を介してかしめることにより取り付けられ、それぞれ負極リード11および正極リード12を介して負極1あるいは正

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極2と電氣的に接続され、電池の負極あるいは正極として機能するように構成されている。なおセパレータは多孔性の膜である。

【0038】この電池では、正極リード12は、電流遮断用薄板8を介して電池蓋7との電氣的接続がはかられていてもよい。このような電池では、電池内部の圧力が上昇すると、電流遮断用薄板8が押し上げられ変形し、正極リード12が上記薄板8と溶接された部分を残して切断され、電流が遮断されるようになっている。

【0039】このような負極1を構成する負極活物質としては、金属リチウム、リチウム合金、リチウムイオンをドーブ・脱ドーブすることが可能な炭素材料のいずれを用いることができるが、これらのうちで、リチウムイオンをドーブ・脱ドーブすることが可能な炭素材料を用いることが好ましい。このような炭素材料は、グラファイトであっても非晶質炭素であってもよく、活性炭、炭素繊維、カーボンブラック、メソカーボンマイクロビーズ等あらゆる炭素材料が用いられる。

【0040】本発明では、特にX線解析で測定した(002)面の面間隔(d002)が0.37nm以下であり、密度が1.70g/cm³以上である黒鉛に近い性質を有する炭素材料が望ましく、このような炭素材料を使用すると、電池のエネルギー密度を高くすることができる。

【0041】また正極2を構成する正極活物質としては、MoS₂、TiS₂、MnO₂、V₂O₅などの遷移金属酸化物および遷移金属硫化物、またはLiCoO₂、LiMnO₂、LiMn₂O₄、LiNiO₂等のリチウムと遷移金属とからなる複合酸化物を用いられ、特にリチウムと遷移金属とからなる複合酸化物が好ましい。

【0042】また、本発明に係る非水電解液二次電池は、図2に示すようなコイン型非水電解液二次電池にも適用することができる。図2のコイン型非水電解液二次電池では、円盤状負極13、円盤状正極14、セパレータ15およびステンレスの板17が、負極13、セパレータ15、正極14、ステンレスの板17の順序で積層された状態で電池缶16に収納され、電池缶(蓋)19がガスケット18を介してかしめることにより取り付けられている。負極13、セパレータ15、正極14としては、前記と同様のものが使用される。また電池缶16、電池缶(蓋)19は、電解液で腐食しにくいステンレスなどの材質のものが使用される。

【0043】なお、本発明に係る非水電解液二次電池は、電解液として以上説明した非水電解液を含むものであり、電池の形状などは図1および図2に示したものに限定されず、角型などであってもよい。

【0044】

【発明の効果】本発明に係る非水電解液は、難燃性であり充放電性能に優れ、このような非水電解液を用いた非水電解液二次電池は、安全で、高電圧を発生でき、充放電特性に優れる。

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【0045】

【実施例】以下、実施例を挙げて本発明を具体的に説明するが、本発明はこれら実施例により何ら限定されるものではない。

【0046】

【実施例1】＜非水電解液の調製＞LiPF₆15.2g(100mmol)を、エチレンカーボネート(EC)とジメチルカーボネート(DMC)とリン酸トリメチル(TMPA)との混合溶媒(混合体積比EC:DMC:TMPA=33.25:61.75:5.0)に溶解してのち、非水電解液中のビニレンカーボネート濃度が0.1重量%となるように添加し、非水電解液を調製した(電解液濃度1.0mol/リットル)。

【0047】＜負極の作製＞まず、負極13を以下のようにして作製した。(株)ベトカ製のメソフェーズピッチマクロファイバー(商品名:メルブロンミルド、d002=0.336nm、密度2.21g/cm³)の炭素粉末95重量部と、結着剤のポリフッ化ビニリデン(PVDF)5重量部とを混合し、溶剤のN-メチルピロリドンに分散させ、負極合剤スラリー(ペースト状)を調製した。

【0048】この負極合剤スラリーを厚さ20μmの帯状銅箔製の負極集電体に塗布し、乾燥させた、帯状の炭素電極を得た。このような炭素電極合剤の厚さは、25μmであった。さらにこの帯状電極を直径15mmの円盤状に打ち抜いた後、圧縮成形し負極13とした。

【0049】＜正極の作製＞正極14は、以下のようにして作製した。本庄ケミカル(株)製のLiCoO₂(製品名:HLIC-21、平均粒径8μm)91重量部と、導電材のグラファイト6重量部と、結着剤のポリフッ化ビニリデン3重量部とを混合して正極合剤を調製し、N-メチルピロリドンに分散させることにより、正極合剤スラリーを得た。

【0050】このスラリーを厚さ20μmの帯状アルミニウム箔製正極集電体に塗布し、乾燥させ、圧縮成形して、帯状正極を得た。このような正極の合剤厚は40μmであった。さらにこの帯状電極を直径15mmの円盤状に打ち抜くことにより正極電極14とした。

【0051】＜電池の作製＞このようにして得られた円盤状負極13、円盤状正極14、およびセパレータ15(厚さ25μm、直径19mmの微多孔性ポリプロピレンフィルム)を図2に示すように、ステンレス製の2032サイズの電池缶16に、負極13、セパレータ15、正極14の順序で積層したのち、セパレータ15に前記非水電解液を注入した。その後、ステンレス製の板17(厚さ2.4mm、直径15.4mm)を収納した後、ポリプロピレン製のガスケット18を介して、電池缶(蓋)19をかしめることにより、電池内の気密性を保持し、直径20mm、高さ3.2mmのボタン型非水電解液二次電池を作製した。

50 - 【0052】＜放電容量および負荷特性の測定＞このよ

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うにして作製した非水電解液二次電池の放電容量を測定した。なお、本実施例では、負極にLi⁺がドーブされる電流方向を充電、脱ドーブされる電流方向を充電とした。

【0053】充電は、4.2V、1mA定電流定電圧方法で行い、充電電流が50 μ A以下となった時点で終了とした。放電は、1mAの定電流で行い、電圧が2.7Vに達した時点で終了とした。この充放電サイクルの充電容量と放電容量とから、次式により充放電効率を測定した。結果を表1に示す。

【0054】

【数1】

$$\text{充放電効率}(\%) = \frac{\text{放電容量(mAh/g)}}{\text{充電容量(mAh/g)}} \times 100$$

【0055】<非水電解液の自己消火性評価>前記非水電解液の入ったビーカー中に、15mm、長さ30cmの短冊状に切断した厚さ0.04mmのセパレーター用マニラ紙を1分以上浸した。マニラ紙から滴り落ちる過剰の非水電解液をビーカー壁で拭い、マニラ紙を2.5cm間隔で支持針を有するサンプル台の支持針に刺して水平に固定した。マニラ紙を固定したサンプル台を25cm \times 25cm \times 50cmの金属製の箱に入れ、一端をライターで着火し、セパレーター紙の燃えた長さを測定し、燃焼長が1cm未満の場合を自己消火性があると評価した。

【0056】結果を表1に示す。

【0057】

【実施例2】実施例1において、ビニレンカーボネートの添加量を0.5重量%とした以外は、実施例1と同様に、電池の充放電効率および非水電解液の自己消火性を評価した。

【0058】結果を表1および図3に示す。

表1

	非水溶媒組成(体積比)			ビニレンカーボネート添加量(重量%)	充放電効率 %	自己消火性
	EC	DMC	TMPA			
実施例1	33.25	61.75	5.0	0.1	91.9	あり
実施例2	33.25	61.75	5.0	0.5	94.1	あり
実施例3	33.25	61.75	5.0	0.5*	92.2	あり
実施例4	33.95	63.05	3.0	0.5	94.9	あり
実施例5	32.55	60.45	7.0	0.5	91.7	あり

* 実施例3では、4,5-ジメチルビニレンカーボネートを使用した。

【図面の簡単な説明】

【図1】本発明の非水電解液二次電池の一実施例を示す円筒型電池の概略断面図である。

【図2】本発明の非水電解液二次電池の一実施例を示すコイン電池の概略断面図である。

【図3】本発明の実施例および比較例におけるTMPA

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* 【0059】

【実施例3】実施例1において、ビニレンカーボネートの代わりに、4,5-ジメチルビニレンカーボネートを使用し、かつその添加量を0.5重量%とした以外は、実施例1と同様に、電池の充放電効率および非水電解液の自己消火性を評価した。

【0060】結果を表1に示す。

【0061】

【実施例4】LiPF₆15.2g(100mmol)を、エチレンカーボネート(EC)とジメチルカーボネート(DMC)とリン酸トリメチル(TMPA)との混合溶媒(混合体積比EC:DMC:TMPA=33.95:63.05:3.0)に溶解したのち、非水電解液中のビニレンカーボネート濃度が0.5重量%となるように添加し、非水電解液を調製した(電解質濃度1.0mol/リットル)。得られた非水電解液を用いて、実施例1と同様に電池の充放電効率および非水電解液の自己消火性を評価した。

【0062】結果を表1および図3に示す。

【0063】

【実施例5】LiPF₆15.2g(100mmol)を、エチレンカーボネート(EC)とジメチルカーボネート(DMC)とリン酸トリメチル(TMPA)との混合溶媒(混合体積比EC:DMC:TMPA=32.55:60.45:7.0とし、非水電解液中のビニレンカーボネート濃度が0.5重量%となるように添加し、非水電解液を調製した(電解質濃度1.0mol/リットル)。得られた非水電解液を用いて、実施例1と同様に電池の充放電効率および非水電解液の自己消火性を評価した。

【0064】結果を表1および図3に示す。

【0065】

【表1】

に対する充放電効率の変化を表す図である。

【符号の説明】

1,13・・・負極

2,14・・・正極

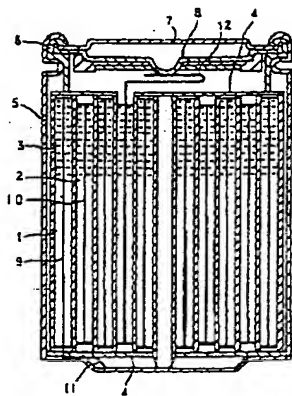
3,15・・・セパレータ

4・・・絶縁板

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- 5, 16 電池缶
 6 封口ガスケット
 7 電池蓋
 8 電流遮断用薄板
 9 負極集電体
 10 正極集電体

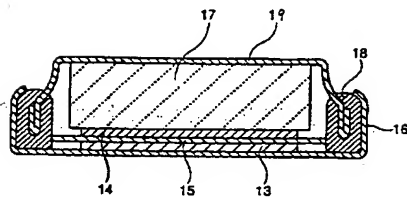
【図1】



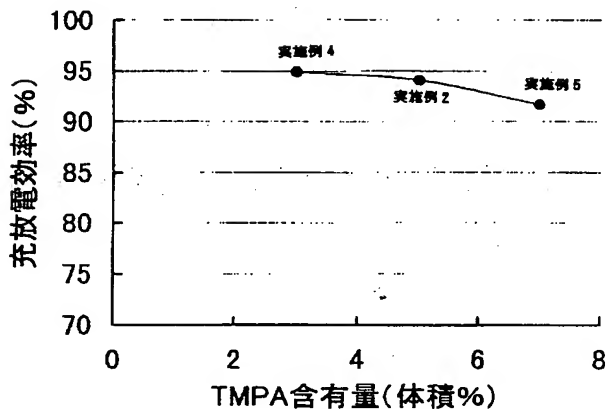
14

- 11 負極リード
 12 正極リード
 17 ステンレス製の板
 18 ガスケット
 19 電池缶 (蓋)

【図2】



【図3】



フロントページの続き

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